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Distortional Isomers of a Mixed-Valence Binuclear Cu Complex

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Binuclear copper complexes have important functional roles in many metalloproteins,[1] a noteworthy example being cytochrome *c* oxidase, whose resting state contains a mixed-valence Cu_2 site,[1,2] the Cu_A center. The importance of direct Cu−Cu bonding in this protein site remains unclear at this time. The work reported here demonstrates that the Cu−Cu bonding interaction in a model binuclear complex is strongly mediated by ligand environment,[3] and the weakness of this Cu−Cu bond may have functional significance for the Cu_A center.

Numerous model $(Cu_2)^{n+}$ complexes have been prepared.[3−5] Our current investigation focuses upon the exceptionally thermally stable complex $[Cu_2(L)]^{3+}$ (L = $N(CH_2CH_2N(H)CH_2CH_2N(H)CH_2CH_2)_3N$), **1**,[5] which contains a Cu_2^{3+} unit stabilized by encapsulation in the octaaza-cryptand ligand L. This complex exhibits optical absorption and MCD spectra that are quite similar to those of the Cu_A center of resting cytochrome oxidase.[4e] EPR data established a delocalized ($Cu^{1.5}$) valence state for this complex under a variety of conditions, and crystallographic Cu_2 distances of 2.364(1) and 2.415(1) Å determined for the nitrate and acetate salts of this cation are consistent with very substantial metal−metal interaction. This contrasts markedly with $d(Cu_2)$ = 2.616(1) Å determined for the prototypical binuclear Cu(II) compound $Cu_2(acetate)_4)(OH_2)_2$.[6]

Resonance Raman (RR) spectra of **1** have been obtained over a range of excitation wavelengths for two forms of crystalline solids and various solution species. The complex absorbs intensely in the red and near-infrared spectral regions. Electronic absorption spectra in aqueous solution ($\lambda_{max}(\epsilon_{max})$: 622 (3350); 748 (5600); 1000 nm (∼1200 M^{-1} cm^{-1}, sh)) and nonaqueous solution (CH_3OH, CH_3CN, dimethylformamide, CH_2Cl_2, etc.) and also of solid samples (diffuse reflectance) are all similar, although the intensity of the ≈750 nm absorption band depends on solvent polarity. The RR spectrum (Figure 1B) of the structurally well-defined crystalline nitrate salt of **1** exhibits two intense peaks at about 289 and 172 cm^{-1}, hereafter referred to as ν_1 and ν_2. The

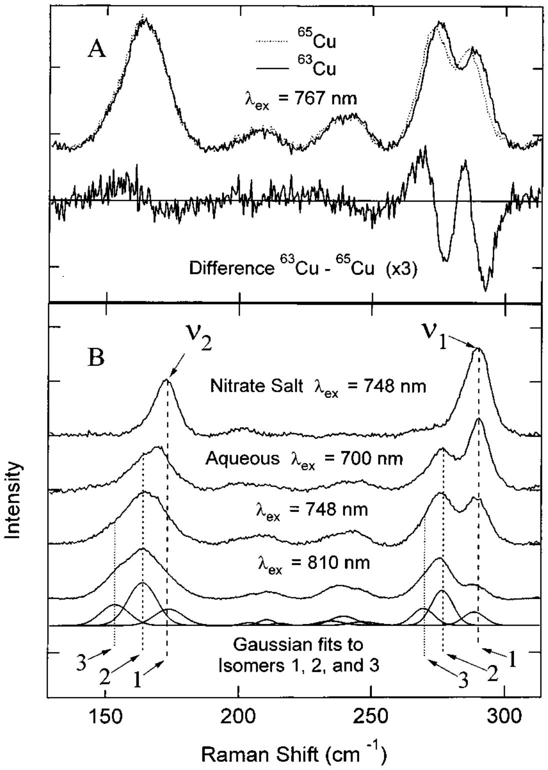

Figure 1. Resonance Raman spectra of $[Cu_2(N(CH_2CH_2N(H)CH_2CH_2N(H)CH_2CH_2)_3N)]^{3+}$. (A) The $^{63}Cu/^{65}Cu$ isotope effect is shown by comparison of two spectra, and by the difference spectrum in the lower trace. The bands that belong to isomers of ν_1 show similar isotopic shifts of 2.5 cm^{-1}, and the bands that belong to ν_2 show a smaller isotopic shift of 0.7 cm^{-1}. (B) A resonance Raman spectrum of the solid nitrate salt of **1** is shown with Raman spectra of the aqueous solutions at a variety of wavelengths. In the spectrum of the nitrate salt of **1**, the Raman bands ν_1 and ν_2 appear as single peaks near 289 and 172 cm^{-1}, respectively. In aqueous solutions, the spectral line shape of the Raman bands ν_1 and ν_2 can be fit with three Gaussian bands as indicated by a fit to the 810 nm data shown in the lowest trace. The three populations of ν_1 have frequencies of 289, 276, and 267 cm^{-1}. The frequencies of ν_2 are 173, 164, and 154 cm^{-1}. The Raman spectra were obtained with an argon ion laser pumped Ti:sapphire laser. The scattered Raman light was collected using lenses and dispersed using a SPEX 1807 triple monochromator/spectrograph, and then detected using a liquid nitrogen cooled Princeton Instruments CCD camera.

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assignments of ν_1 and ν_2 follow from $^{63/65}$Cu shifts measured in room temperature aqueous solutions of the nitrate salt (Figure 1A). In these spectra, ν_1 and ν_2 appear as multiple bands whose components shift by 2.5 and 0.7 cm^{-1}, respectively. Clearly, ν_1 has a great deal of Cu−Cu stretching character. A valence force field calculation[7] fit to the isotopic data suggests that ν_1 and ν_2 are the $\nu(Cu_2)$ and $\delta(N_{eq}CuCu)$ modes, the potential energy distribution (PED) indicating them to have, respectively, 64% and 77% character of the indicated dominant internal coordinate. The partitioning of $\nu(Cu_2)$ obtained from this calculation is in general agreement with the results of an independent normal mode determination recently performed by McGarvey and co-workers.[8] However, the details of the two calculations differ in that those reported in ref 8 assign independent normal modes to the multiple band features that are here assigned as features of multiple conformational isomers that exist in solution.

To explore this point further, we note that while both ν_1 and ν_2 appear as single RR bands for crystals of **1**, in aqueous solution they consist of a number of closely spaced features whose relative intensities are sensitive to temperature, solvent, and excitation wavelength. This difference suggests the existence of multiple species of **1** in solution. The low-frequency Raman data can be modeled by assuming that each species exhibits a basis spectrum consisting of a set of Gaussian peaks (i.e., each spectrum has a ν_1 peak, a ν_2 peak, and two additional smaller peaks between ν_1 and ν_2) with fixed frequencies, relative intensities, and widths. The spectra obtained at all excitation wavelengths could then be fit simultaneously by varying only the relative amplitudes of these "basis spectra" as a function of wavelength (see Figure 1B for the fit at 810 nm). This procedure requires the coexistence of at least three different species (basis spectra) in aqueous solution, and these basis spectra differ from one another primarily by small, unidirectional frequency shifts of all the peaks. Depolarization ratios of $\approx ^1/_3$, determined in aqueous solution for ν_1 and ν_2 with 760 nm excitation, indicate that the vibrational modes are totally symmetric and that the electronic absorption is polarized along the Cu−Cu axis (molecular z axis).[7]

There are several clues available as to the origin of the multiple-component solution RR spectra of **1**. First, both the acetate and nitrate salts exist as crystallographically well-defined structures[5] that each display ν_1 and ν_2 as single-component peaks. However, their band positions differ by ≈2−3 cm^{-1}, with the energies of the nitrate peaks corresponding to the highest frequency basis spectrum in Figure 1B and the acetate peaks being at lower frequency. The direction of this shift is consistent with the increase of the Cu−Cu bond length in the acetate salt by 0.05 Å relative to the nitrate salt,[5] although its magnitude is significantly smaller than predicted by simple diatomic models.[7] Second, the ligand L is very flexible and exhibits variable conformations in response to its environment. For instance, the crystal structure of the hydrated free ligand displays a $(N_3)_{eq}-(N_3)_{eq}$ interplanar distance of 2.98 Å,[9] 0.29 Å larger than that of **1**$(acetate)_3 \cdot 6H_2O$.[5] Third, the RR spectra are strongly influenced by changing the hydrogen-bonding environment around the ligand. The behavior of ν_1 is instructive in this context. The complete absence of hydrogen bonding, achieved by dissolving the $B(C_6H_5)_4^-$ (tetraphenylborate, TPB) salt of **1** in CH_3CN solution, also leads to a Raman spectrum having a single-component ν_1 peak, but at a frequency of 275 cm^{-1}.[7] Aqueous solutions, where hydrogen bonding to the ligand is likely dominated by the solvent, produce identical multicomponent spectra for the acetate and nitrate salts. A different hydrogen-bonding environment is obtained by dissolving the acetate salt of **1** in CH_3CN.[7] In these solutions, ν_1 displays two dominant components, one at 288 cm^{-1} and one at 276 cm^{-1}.

To understand these observations, we suggest that the weakness of the Cu−Cu bond is a key factor. The noteworthy paucity of examples of unbridged binuclear Cu complexes suggests that the Cu−Cu potential surface is quite soft (possibly as a result of state crossings as the metal−metal coordinate is stretched).[10] Accordingly, as is supported by the direct correlation of $d(Cu_2)$ with $d(N_3)_{eq}$ in the two crystal structures,[4,11] the metal−metal potential energy minimum is extremely sensitive to ligand perturbation. Thus, the three discrete basis spectra derived from solution spectra arise from distinct conformational isomers of L influenced by hydrogen-bonding interactions with the solvent. The energy difference between the different isomers is less than 0.6 kcal/mol, and the barriers to interconversion have an upper bound of 20 kcal/mol based on rapid appearance of isomers upon solvation of crystalline **1**. The multicomponent RR bands indicate that a shallow Cu−Cu potential surface leads to differing $d(Cu_2)$ in aqueous solution and a corresponding change in electronic properties for different isomers.[12]

"Bond-stretch" isomers have been largely discredited as a class because structural data upon which the concept was originally based were flawed by unrecognized disorder problems.[13] Bond-stretch isomerism coupled to ligand deformation or distortional isomerism is recognized as a viable mechanism for multiple minima,[14] but evidence for such isomers coexisting as true minima in solution (rather than as "snapshots" captured by individual crystal structures) has been largely lacking. We believe that the present results illustrate a real example of this phenomenon. Moreover, the existence of such isomerism may have important ramifications for the functionality of metal dimers. We note that the softness of the Cu−Cu bonding interaction is a key element leading to the control of Cu−Cu distance, and electronic interaction, by the ligand environment. In cytochrome oxidase, the possibility of such control by subtle changes in the ligand environment could be critically important in the function of the Cu_A subunit, which serves to shuttle electrons to the enzyme's catalytic site. Possibly, the large Debye−Waller terms found by EXAFS for the binuclear Cu_A center of cytochrome oxidase[2] may have a related explanation. In fact, the possibility for such control may well have influenced the development of a binuclear Cu structural motif for this center.

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Supporting Information Available: Details of the normal coordinate analysis, spectral assignments, and additional isotope data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The ≈750 nm absorption band of **1** can be fit by a sum of three Gaussian bands. These may correspond to the three components shown in the fit (bottom trace of Figure 1) consistent with the Raman excitation profile (data not shown).

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